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Rapidly Solidified Copper-Phosphorus Base Brazing Foils

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New copper-phosphorus brazing filler metals are potential replacements for silver-bearing filler metals in copper and copper alloy brazing applications

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Recently, new and improved brazing filler metals have been produced by rapid solidification (Refs. 1,2). The rapidly solidified materials, typically cast in foil form for direct use in metal joining, offer superior chemical and microstructural homogeneity when compared to conventionally formed filler metals. This homogeneity, in turn, results in more uniform melting, flow in the joint area, and solidification during the brazing process. Moreover, rapid solidification offers the formability of foil in many filler metal systems that are brittle and unformable in the crystalline state.

Rapidly solidified nickel-base filler metals of American Welding Society BNi classification (Ref. 3) and new nickel-palladium-base alloys (Ref. 4) are currently being used for various aerospace and electronic applications as replacements for gold-base brazing alloys. This study introduces a new family of rapidly solidified copper-phosphorus-base alloys designed for brazing copper and copper alloys. These new Cu-Ni-Sn-P alloys, designated hereinafter as MBF 2000P series, are potential replacements for commonly used silver-containing filler metals such as BCuP-5 and BAg-1 (Ref. 5).

These new alloys have near-eutectic compositions in the quaternary Cu-Ni-Sn-P system. The nominal compositions of the two candidate alloys, MBF 2002P and 2005P, are shown in Table 1. These silver-free alloys offer reduced raw material costs compared to conventional silver-bearing alloys. In addition, they do not contain toxic cadmium, usually added to the BAg series as a melting point depressor. The high phosphorus content makes them self-fluxing but does not pose a problem for foil fabrication. Flexible and homogeneous foils are fabricated directly by rapid solidification.

Potential applications of these alloys can range from brazing of heat exchangers and specialty plumbing fixtures to electrical contact brazing. Hence, brazed joint characteristics such as mechanical strength, toughness and electrical resistance are important considerations for a comparative study. Similarly, flow and wetting characteristics, or "brazability," of these new alloys should be compared with those of conventional silver brazing filler metals.

This paper summarizes the performance characteristics of two new copper/phosphorus-base rapidly solidified brazing filler metals, designated 2002P and 2005P, and compares them with those of conventional silver-bearing alloys, BCuP-5 and BAg-1, in brazing copper. Compared are melting behavior and wetting characteristics of the filler metals. Important characteristics of copper/copper brazed joints germane to mechanical and electrical applications—*e.g.*, tensile, shear and impact strengths and electrical resistance—are examined in detail. In addition, the effects of nickel and tin on brazed joint mechanical properties and joint morphology are examined.

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Experimental Procedure

Ribbon Casting

Brazing filler metal foils or ribbon samples were fabricated by rapid solidification. The Cu-Ni-Sn-P alloys, shown in Table 1, were cast directly from the liquid state into nominally 1 or 2 in. (25 or 50 mm) wide and 0.001 in. (0.025 mm) thick ribbons. According to this process, a sheet of molten alloy was ejected through a rectangular slot onto a rotating chill block (Ref. 6) and quenched at a rate ~10^6°C/sec (~18^6°F/sec), yielding a homogeneous amorphous brazing filler metal foil. These foils are flexible and can be punched or cut into brazing preforms.

Differential Thermal Analysis

Liquidus and solidus of the alloys were determined with a Perkin Elmer Differential Thermal Analyzer (DTA) in an inert atmosphere, using a heating rate of ~20°C/min (36°F/min). From the DTA thermograms, one can estimate the beginning and completion of melting, known respectively as solidus and liquidus (Ref. 7).

Wetting Characteristics

The ease of brazing depends primarily on the wetting characteristics of the filler metal used. A standard test to

Table 1—Composition of Cu-P Base Brazing Filler Metals Produced by Rapid Solidification

Alloy Designation	Nominal Composition, Wt-% Cu	Ni	Sn	P
MBF 2002P	78	10	4	8
MBF 2005P	77	6	10	7

35/02 D, amorph.

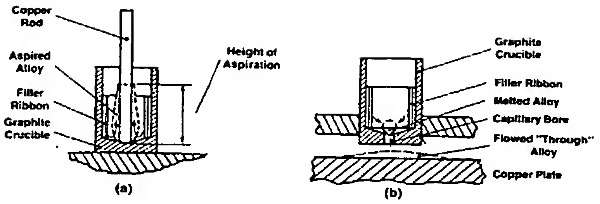


Fig. 1—Experimental setup for aspiration test (a) and flow-through test (b)

evaluate wetting characteristics of different filler metals does not exist. However, there are wettability tests, reported in the literature, which have been used for comparative estimation of wetting characteristics. The four tests described below were employed to compare wetting characteristics of 2002P, 2005P, BCuP-5 and BAg-1.

Flow Test. This test, widely used in brazing and soldering, consists of placing identical samples of brazing filler metals on a base metal and heating the whole assembly to the brazing temperature (Ref. 8). The area across which the molten alloy spreads is an indication of flowability. The test was conducted by placing equal volumes of 2002P, 2005P, BCuP-5 and BAg-1 foils on a copper plate and heating the whole assembly at 740°C (1365°F) for 5 minutes in an argon atmosphere.

Aspiration Test. The procedure described in Ref. 9 was modified to perform the test with a small quantity of filler metal. Equal volumes (80 mm^3/0.005 cu. in.) of wrapped brazing ribbon were placed in analytical grade graphite crucibles—Fig. 1a. Each crucible was fitted with a copper rod positioned vertically along the crucible axis. The crucible/filler metal/copper rod assemblies were heated at 740° and 800°C (1365° and 1470°F) for 5 minutes in an argon atmosphere. The aspiration heights of the molten filler metals, which depend on their wetting characteristics on copper, were recorded by examining these copper rods under a microscope.

Flow-Through Test. A qualitative evaluation of filler metal surface tension can be made by examining the flow of a small volume of molten filler metal through a narrow orifice at the bottom of a graphite crucible. If a piece of ribbon sample is placed in a graphite crucible and heated above its liquidus, the sample, at first, melts and forms a spherical droplet. Beyond a certain superheat temperature, the molten alloy surface tension becomes insufficient to support the liquid droplet, and it flows through the orifice. If the hydrostatic pressure at the orifice is kept constant, the temperature at which the droplet begins to flow is indicative of the surface tension of the molten filler metal; a low flow-through temperature indicates a low surface tension.

The flow-through tests were conducted at two temperatures, 740° and 800°C (1365° and 1470°F). About 80 mm^3 (0.005 cu in.) of wrapped ribbon was inserted into a crucible (Fig. 1b) of 9 mm (0.350 in.) ID with a 1.6 mm (0.063 in.) orifice diameter at the bottom of the crucible. The crucibles with filler metals were positioned ~2 mm (0.079 in.) above a copper plate. The crucible/plate assembly was placed into a furnace and heated in a nitrogen atmosphere to examine the flow behavior.

Measurement of Dihedral Angles At Grain Boundaries. Dihedral angles were measured from the microstructures of copper-to-copper joints brazed with 2002P, 2005P, BCuP-5 and BAg-1 filler metal (Ref. 10).

Brazing Techniques

Torch Brazing. Figure 2 illustrates a typical sequence of

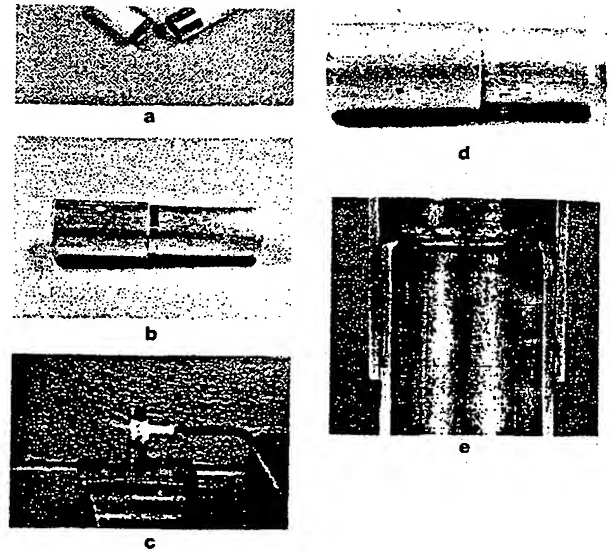


Fig. 2—Sequence of torch brazing using 2000P foil

torch brazing copper tubes with 2000P series ribbon samples. Parts to be brazed, with brazing foil placed in between, were held together by appropriate fixturing. Usually, two pieces of nominally 25 μm (1 mil) thick foils were placed at the joint to provide an adequate supply of filler metal during brazing. An oxyacetylene torch was used for brazing. A No. 5 torch tip was used and the oxygen and acetylene pressures were set at 34.5 kPa (5 psi). Acetylene flow was adjusted to make the flame slightly reducing. The joint was heated without any flux until the filler metal began to melt and flow.

Furnace Brazing. Furnace brazing was conducted in a nitrogen atmosphere. The majority of test samples—mechanical, electrical and corrosion—were brazed by this technique. Furnace brazing can be used for many prefixtured parts, such as heat exchangers or electrical contact parts.

Shear test samples with appropriate filler metals were placed in a special fixturing jig—Fig. 3. The jig holds the samples together and maintains a preselected joint clearance with the help of shim stocks and wedges. Butt joint samples for tensile and impact tests were fixtured by laser beam tack

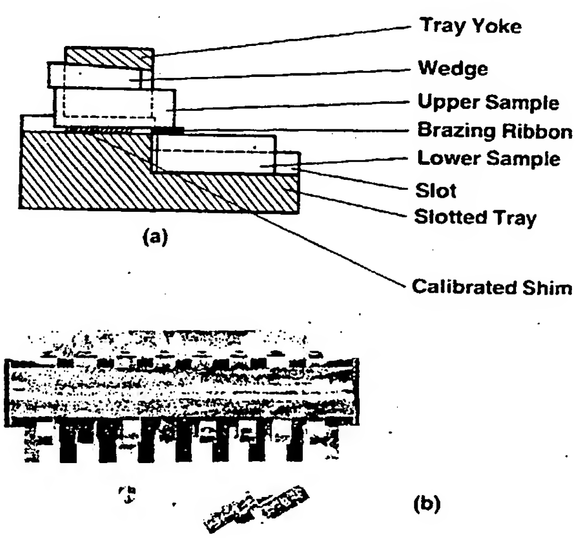


Fig. 3—Brazing tray fixture for shear test sample—(a) cross-section, (b) plan (photo)

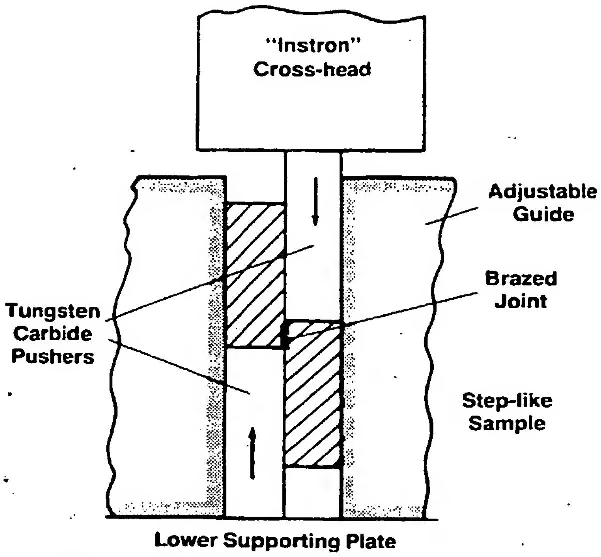


Fig. 4 — Schematic arrangement of shear test

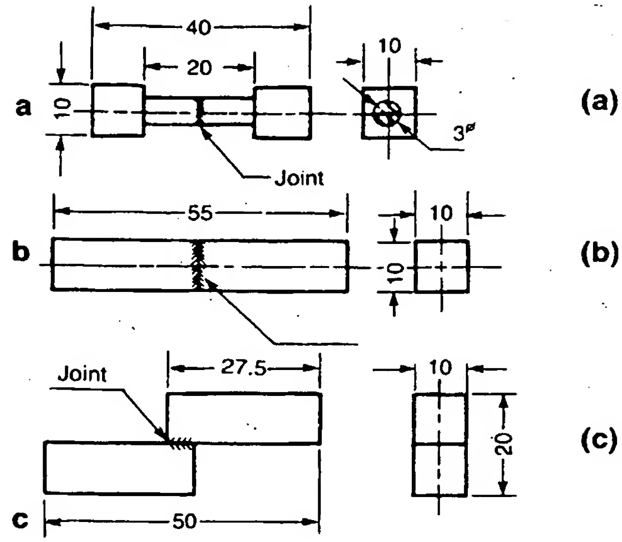


Fig. 5 — Dimensions of test samples used for measurements of (a) joint resistance, (b) impact strength and (c) shear strength. (All sizes in mm)

welding two test pieces with the brazing foil placed in the joint. In this case, the brazing foil acted as the spacer.

The majority of the joints were brazed with two 25 μm (1 mil) thick foil inserts. To ensure an adequate amount of filler metal, some excess foil extending ~3 mm (⅛ in.) beyond the joint edges was provided. The fixtured assemblies were placed in a retort furnace with nitrogen continuously flowing through the retort. Brazing temperatures were typically 100°C (180°F) above the filler metal liquidus. The sample temperature was monitored by a thermocouple in direct contact with the sample.

Mechanical Testing

An Instron tensile testing machine was employed to determine joint tensile strength of brazed butt joints. Standard AWS C3.2 lap-shear (Ref. 11) samples made of 3 mm (0.118 in.) plates were found inappropriate for testing soft copper, as joints developed a triaxial stress situation due to localized deformation of copper in the vicinity of the brazed joint. Therefore, approximately 1 cm (0.4 in.) square copper bars were used for brazing shear and impact test samples.

After brazing, impact samples were ground to 1 cm (0.4 in.) square cross-sections. The brazed joint provided a suitable notch. The samples were Charpy impact tested to determine the brazed joint toughness. For the shear test, a compressive (instead of tensile) load was used. Samples were placed in a special device providing a strong lateral support, and the compressive load was applied via tungsten carbide pushers (Fig. 4), using a standard Instron machine. Brazed joints, in this configuration, are subjected to only shear stress components because rotating moments and normal components are balanced by lateral constraints. As a result, shear stress values represent the true joint shear strengths, independent of joint overlap and triaxiality. Figure 5 illustrates dimensions of the mechanical test samples.

Metallography

Metallographic samples were prepared to examine the effects of filler metal composition and brazing conditions on the microstructure of brazed joints. Special care (Ref. 12) was taken to preserve the joint morphology and eliminate artifacts resulting from preferential removal of hard phases. Both optical and scanning electron microscopy, including elemental mapping, were employed whenever necessary.

Joint Electrical Resistance

Brazed butt joints in 1 cm (0.4 in.) square copper bars were machined to cylindrical shafts of 2-3 mm (0.079-0.118 in.) diameter. Control samples of the same shape were prepared from unbrazed copper bars and were subjected to heat treatments together with brazed assemblies in order to compare resistivities after identical treatments.

A four-probe method employing a high impedance digital microvoltmeter was used to measure such low resistance values of copper samples. Figure 6 illustrates the instrument layout. Resistance of a constant-length sample containing the brazed joint was measured using tungsten carbide probes. The increase in sample resistance (ΔR) due to the brazed joint was derived by subtracting the resistance of the control copper sample from that of the brazed sample.

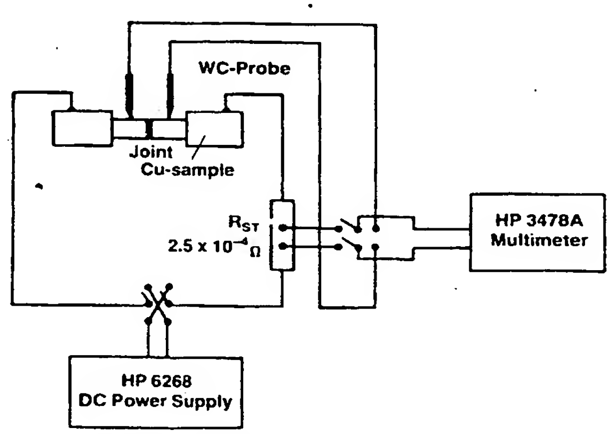


Fig. 6 — Schematic diagram of instrument setup for measuring brazed joint electrical resistance

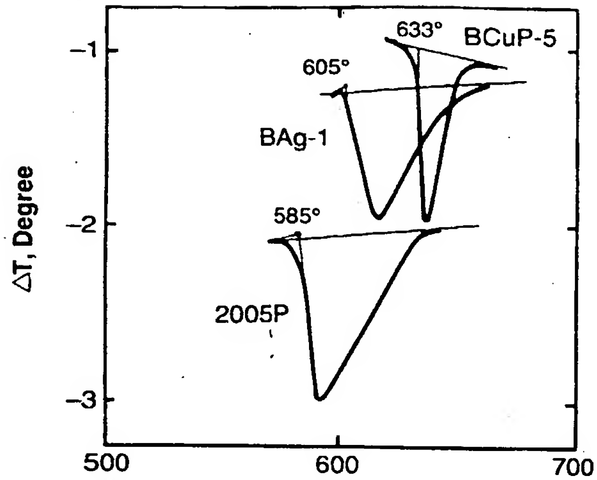


Fig. 7—DTA scans of 2005P, BAg-1 and BCuP-5

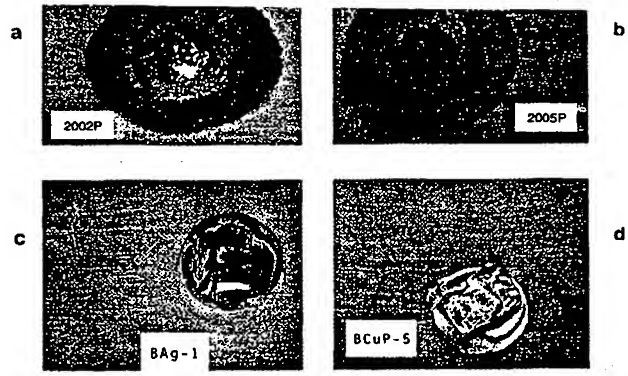


Fig. 8—Behavior of brazing filler metal during flow test. Samples were placed on flat copper plates and then heat treated at 740°C for 5 minutes. Only 2002P and 2005 P have flowed. (X4)

Results and Discussion

Melting Characteristics

Figure 7 illustrates DTA scans of 2005P, BAg-1 and BCuP-5 brazing filler metal at a heating rate of 20°C/min (36°F/min). The solidus and liquidus, t_s and t_f, are determined by drawing tangents at the two shoulders of the melting trough (Ref. 7). Single melting trough thermograms observed for all three filler metals represent a near-eutectic or congruent melting behavior. Because of the thermal inertia of a finite sample size and the dynamic nature of the experiment, the thermograms exhibit a melting range rather than a unique equilibrium melting temperature. Consequently, there exists a controversy regarding what temperature, t_s, t_{trough} or t_f should be chosen as the equilibrium melting temperature (Ref. 7). In the present study, t_s and t_f are referred to as solidus and liquidus, respectively. Dynamic experimental conditions, however, more closely simulate brazing cycles generally employed, making a melting range rather than a unique temperature of greater practical significance. The melting range was found to be relatively insensitive to the heating rates (2°-20°C/min, or 3.6°-36°F/min) examined in the present study. A maximum variation of 10°-15°C (18°-27°F) was observed. All the DTA scans in the present study were determined at a 20°C/min (36°F/min) heating rate.

Table 2 illustrates t_s and t_f of four brazing filler metals. For BAg-1 and BCuP-5, manufacturer's catalog data are also shown in parentheses. It is evident that melting ranges of 2002P and 2005P are identical to those of high silver containing BAg-1. The melting range of low silver BCuP-5 is about 50°C (90°F) higher. However, if trough temperatures in Fig. 7 are compared, 2005P exhibits the lowest temperature, ~80°C (144°F) lower than BAg-1 and ~110°C (198°F) lower than BCuP-5. This lower melting range of 2000P series will enable brazing to be performed at a lower temperature and, therefore, can be a source of potential energy and other related cost savings.

Wetting Characteristics

This study did not attempt an accurate estimation of surface tension values of filler metals. Instead, several convenient tests were selected to qualitatively compare the overall wetting behavior of the four filler metals on a copper surface.

Flow Test. Figure 8 illustrates flow or spreading characteristics of 2000P series and standard silver-containing brazing filler metals after heating at 740°C (1365°F) for 5 minutes. It is evident that only 2002P and 2005P samples flowed and formed blotted spots of approximately equal size. The BCuP-5 sample exhibited signs of incipient melting, whereas the BAg-1 sample remained essentially unmelted. The unmelted BAg-1 sample showed a considerable weight loss with an attendant increase (100°C/180°F) in liquidus. The weight loss of BAg-1 was found to be due to the evaporation of Zn and Cd.

Aspiration Test. With a 5 minute holding time at 740°C (1365°F), all three phosphorus-containing filler metals—2002P, 2005P and BCuP-5—melted and, through capillary action, rose up the copper rod; BAg-1 did not melt and experienced a weight loss. The aspiration heights due to capillary action for different filler metals are listed in Table 3

Table 2—Melting Characteristics of MBF 2000P Alloys And Common Silver-Containing Filler Metals

Alloy Designation and Source	Alloy Nominal Composition, wt.-%	Melting Range Solidus (°C)	Melting Range Liquidus (°C)
MBF 2002P Metglas Products	Cu78Ni19Sn4P8	610	645
MBF 2005 Metglas Products	Cu77Ni6Sn10P7	585	647
Easy Flo 45 (BAg-1) Engelhard	Ag45Cu15Zn16Cd24	605 605[a]	650 620[a]
Met. Braze 15 (BCuP-5) Metz Met. Corp.	Ag15Cu80P5	633 640[a]	680 705[a]

[a]According to Engelhard and Metz Met. Data Sheet.

Table 3—Aspiration Heights of Liquid Brazing Filler Metals on Copper Rods

Alloy Designation	Heat Treatment	Filler Metal Volume, $m^3 \times 10^9$	Aspiration Height, mm
2002P	740°C, N_2 5 min	7.8	10.88
2005P	740°C, N_2 5 min	7.8	10.93
BCuP-5	740°C, N_2 5 min	8.5	11.18[a] (8.55)

[a]BCuP-5 exhibited signs of liquation. Only a very thin film of molten alloy rose up to 11.18 mm by capillary action. Majority of alloy volume was up to 8.55 mm.

Fig. 9—Aspiration or capillary rise of brazing alloys on copper rods after heating for 5 minutes at 740°C in argon (X4)

and illustrated in Fig. 9. It should be noted that BCuP-5 wetted the copper rod nonuniformly, probably due to liquation. Only a small portion of the filler metal, presumably the lower melting component of BCuP-5, rose to the maximum height, with the bulk remaining at the bottom half. Aspiration of 2000P series alloys was quite uniform, as shown in Fig. 9.

Flow-through Test. At 740°C (1365°F), none of the filler m tals flowed through the orifice at the crucible bottom. Only the phosphorus-containing alloys melted and spheroidized into droplets above the capillary hole. The surface tension was large enough to prevent the flow through the orifice. However, at 800°C (1470°F), 2005P flowed through the hole and formed a circular deposit on the copper plate placed beneath—Fig. 10.

Grain Boundary Dihedral Angles. Figure 11 illustrates typical microstructures of copper/copper joints brazed with the four filler metals. Shown in the components of the figure are typical dihedral angles as indicated by arrows. The range and average dihedral angles for the four filler metals are shown in Table 4.

Equilibrium surface tensions on the contact line, where liquid filler metal, solid base metal and gaseous phases co-exist, determine the flowability of a finite volume of a molten filler metal. On a flat surface, this equilibrium is expressed as

$$\sigma_{L/S} + \sigma_{L/G} \cos \Theta - \sigma_{S/G} = 0 \qquad (1)$$

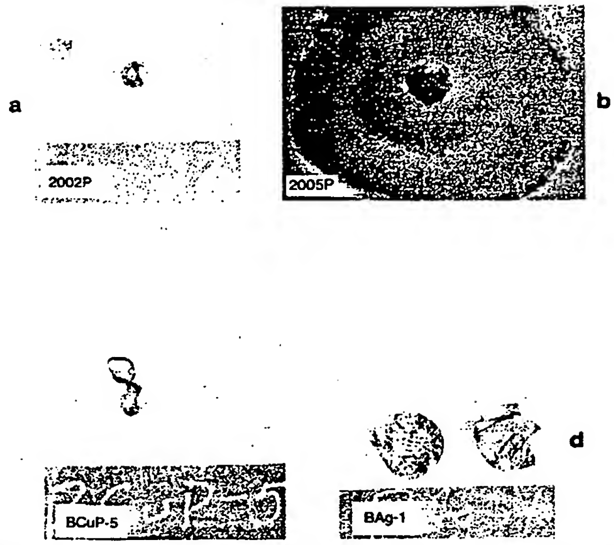


Fig. 10—Results of flow-through test or modified sessile drop method (X4)

where $\sigma_{L/S}$ is the surface tension between liquid filler metal and solid base metal, $\sigma_{L/G}$ is the tension between liquid filler metal and gaseous phases, $\sigma_{S/G}$ is the tension between solid base metal and gaseous phases, and Θ is the contact angle. Good wetting and flow are observed when $\sigma_{L/G}$ and $\sigma_{L/S}$ are smaller than $\sigma_{S/G}$. While several methods have been developed to accurately measure $\sigma_{S/G}$ and $\sigma_{L/G}$ (Ref. 9), direct measurements of $\sigma_{L/S}$ are difficult, particularly in the case of wetting metallic surfaces with a molten filler metal. Substantial interaction of contacting metals results in a nonequilibrium state (Ref. 13).

Capillary rise or aspiration height of a liquid brazing filler metal on a vertically positioned solid base metal depends on the values of $\sigma_{S/G}$ and $\sigma_{L/S}$ and the density of the molten filler metal. A high aspiration height is simply a manifestation of high $\sigma_{S/G}$ and low $\sigma_{L/S}$, assuming alloy densities are nominally

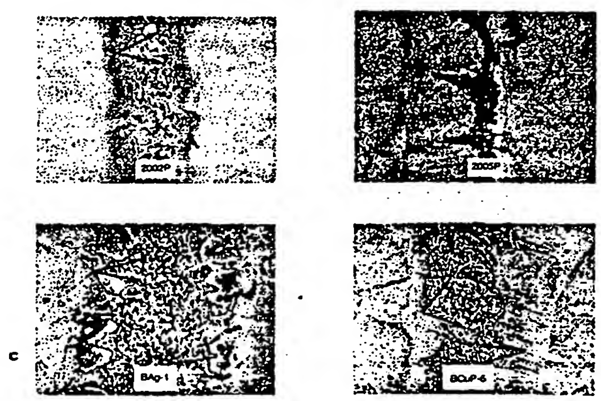


Fig. 11—Typical dihedral angles observed at copper/filler metal interfaces in joints brazed with 2002P, 2005P, BAg-1 and BCuP-5 (X500)

Table 4—Dihedral Angles, Θ_d, Formed at Intersections of Copper Grain Boundaries with Liquid Brazing Filler Metals During Brazing[a]

Alloy Name	Conditions of Brazing	Range of Observed Angles, deg	Average Angle (Θ_d), deg	Cos ($\Theta_d/2$)	Ratio of Surface Tensions, $\sigma_{Cu/L}$ to $\sigma_{Cu/Cu}$
2002P (7 intersections)	740°C, 5 min, Ar	47-90	65	0.84	0.59
2005P (8 intersections)	740°C, 5 min, Ar	5-20	12	0.99	0.50
BCuP-5 (13 intersections)	800°C, 5 min, Ar	20-135	48	0.91	0.55

[a] Here $\cos(\Theta_d/2) = \sigma_{Cu/Cu}/2\,\sigma_{Cu/L}$, where $\sigma_{Cu/Cu}$ is the grain boundary surface tension, which is ~ 1/3 of $\sigma_{Cu/L}$. $\sigma_{Cu/L}$ is the tension of the solid copper free surface (~ 1360 dyn/cm). $\sigma_{Cu/L}$ is the interfacial surface tension on the copper-liquid brazing filler metal interface. *Note:* The smaller the dihedral angle the lower $\sigma_{Cu/L}$ and the better the melting of the copper surface.

Table 5—Comparison of Wetting Characteristics of Copper By Phosphorus-Containing Alloys under Fluxless Heating in a Furnace (Argon and Nitrogen Atmosphere)[a]

Alloy Designation	Flow Test	Aspiration Test	Surface Tension	Dihedral Angle	Overall
2002P	1,2	1	2	3	2
2005P	1,2	2	1	1	1
BCuP-5	3	3	3	2	3

(a) 1—best; 2—medium; 3—poorest.

the same. For good wetting, $\sigma_{L/S}$ should be much less than $\sigma_{S/G}$. Therefore, a high capillary rise insures better wetting. Capillary rise is also important for filling vertical joints and for fillet formation. From Table 2, all three phosphorus-containing alloys exhibited similar aspiration heights (11 mm/0.43 in.) at 740°C (1365°F). However, BCuP-5 showed signs of liquation. The higher melting component remained below 8.55 mm (0.34 in.). Rapidly solidified 2002P and 2005P, being homogeneous, did not stratify and exhibited a uniform capillary effect.

For a polycrystalline body in equilibrium with a liquid with grain boundaries normal to the liquid/solid interface, equation (1) assumes the following special form:

$$\sigma_{S/S} = \sigma_{L/S}/2 \cos (\Theta_d/2) \qquad (2)$$

where $\sigma_{S/S}$ is grain boundary interfacial tension and Θ_d is the dihedral angle. In this study, $\sigma_{S/S}$ is constant. Hence, a lower value of Θ_d reflects better wetting characteristics of the filler metal.

Table 4 lists the average values of Θ_d determined from a large number of brazed joint microstructures, as typically shown in Fig. 11. Only the phosphorus-containing alloys were studied. Within experimental error, BCuP-5 and 2002P have similar values of Θ_d, whereas 2005P has a substantially lower Θ_d, indicating the best wetting characteristics.

An overall comparison of wetting characteristics of the three phosphorus-containing alloys is summarized in Table 5. BAg-1 is not included, as the present experimental conditions, characterized by a slow heating rate, resulted in a substantial loss of Zn and Cd and a corresponding increase in the melting point.

Brazed Joint Mechanical Properties

Tensile Strength. Brazed joint tensile strength was determined by using butt joint specimens, as illustrated in Fig. 5. Table 6 compares brazed butt joint tensile strengths (average of three samples).

Impact Strength. Butt joint samples (Fig. 5) were also tested for impact strength using the brazed joint as a built-in notch. Joint impact strength values are also shown in Table 6.

Shear Strength. Figure 12 illustrates shear strength as a function of joint thickness for joints brazed with 2002P, 2005P and BCuP-5.

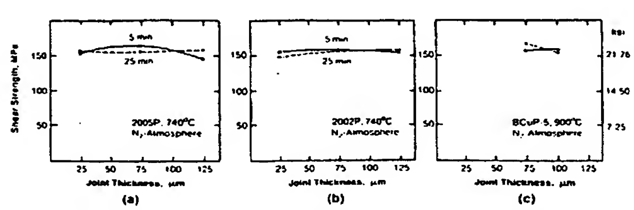


Fig. 12—Shear strength of copper-to-copper joints brazed with 2002P (a), 2005P (b) and BCuP-5 (c) as a function of joint thickness

Table 6—Comparison of Tensile and Impact Strength of Copper-to-Copper Joints Brazed with 2000P Series and Silver-Containing Alloys[a]

Alloys	Joint Tensile Strength (Butt Joint) MPa (psi)[b]		Joint Impact Strength J (Ft lb)[b]	
2002P	110	(16,000)	2.7	(2)
2005P	158.5	(23,000)	14.9	(11)
BCuP-5	193	(28,000)	2.7	(2)
BAg-1	145	(21,000)	9.5	(7)

(a) Joint thickness—75µm (3 mils); brazing temperature—T_L + 100°C; brazing time—5 min in nitrogen.
(b) Average of three samples.

From Table 6, it is evident that BCuP-5 brazed butt joint samples have the highest joint tensile strength. However, they have the lowest impact strength. The 2005P joints, however, have a somewhat lower tensile strength, 159 vs. 193 MPa (23 ksi vs. 28 ksi), but substantially better impact strength, 15 vs. 2.7 J (11 ft lb vs. 2 ft lb). The BAg-1 joints have intermediate tensile strength, 144 MPa (21 ksi) and impact strength, 9.5 J (7 ft lb). The lowest tensile strength was observed for 2002P, 110 MPa (16 ksi). The impact strength of this filler metal is also lower than those of 2005P and BAg-1 but similar to that of BCuP-5. Therefore, 2005P brazed joints appear to have the best combination of tensile and impact strengths, followed by BAg-1, BCuP-5 and 2002P.

Shear strength results indicate a similar trend—Fig. 12. The optimum joint shear strengths for 2002P and 2005P are nearly the same as that for BCuP-5. For a 5 minute brazing time, generally employed in the industry, 2005P has the highest shear strength, 170 MPa (24.3 ksi).

Usually, joint shear strength depends on brazed joint thickness (Ref. 11). There is an optimum thickness for which the shear strength has the highest value. Figure 12 illustrates the effect of joint thickness on shear strength for 2002P, 2005P and BCuP-5 for two brazing times, 5 and 25 min. It is evident that within the thickness range, examined in the present study (25–100 µm, or 1-4 mils), the joint shear strength is relatively insensitive to joint thickness. However, it appears that somewhat higher strength is observed around a thickness of 75 µm (3 mils).

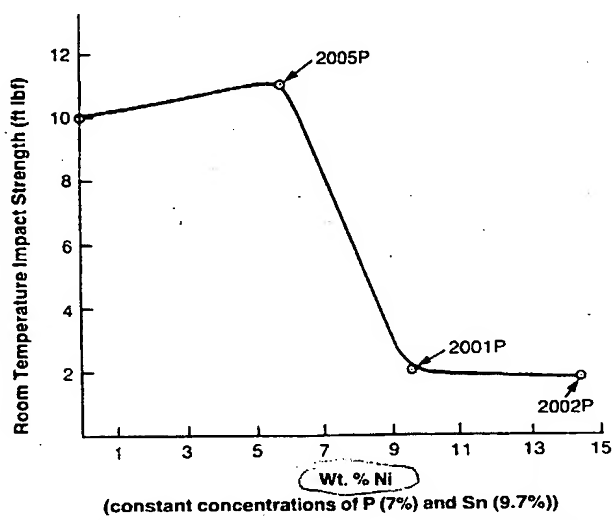


Fig. 13—Variation of brazed joint impact strength as a function of nickel concentration in 2000P alloys

Table 7—Electrical Resistivity and Conductivity of Copper-To-Copper Joints Brazed with 2000P Series and Standard Silver-Containing Alloys

Alloy Designation	Joint Thickness, μm	Joint Electrical Characteristics	
		Resistivity, nohm/m	Conductivity, % IACS[a]
2002P	89	355	4.8
2005P	70	820	2.1
BCuP-5	30	980	1.76
BAg-1	72	90	19

[a]Conductivity (% IACS) is calculated as a percentage of conductivity of pure copper, which is taken as 0.058 nohm^{-1}/m^{-1}.

Table 8—Electrical Resistivity of 2000P Series Filler Metals And Standard Silver-Containing Alloys

Designation	Resisitivity, nohm/m	Conductivity, % IACS[a]
2002P	1500	1.15
2005P	1880	0.91
BCuP-5	150.7[b]	11.9[b]
BAg-1	71.1[b]	24.2[b]

[a]Conductivity (% IACS) is calculated as a percentage of conductivity of pure copper, which is taken as 0.058 nohm^{-1}/m^{-1}.
[b]According to Handy & Harman Data Sheet.

Joint Electrical Resistance

Table 7 illustrates electrical characteristics of copper-to-copper joints brazed with 2002P, 2005P, BCuP-5 and BAg-1. Corresponding filler metal resistivity values are shown in Table 8. It is evident that the conductivity of joints brazed with BCuP-5 is lower than that of the filler metal. In the case of BAg-1, the joint resistance is very close to that of BAg-1 ribbon. The opposite is true for joints brazed with 2002P and 2005P. Being amorphous, the 2000P series filler metals have appreciably higher resistivity than the crystalline BCuP-5 and BAg-1. However, resistivity values of the joints brazed with the 2000P series filler metals are similar to that of BCuP-5, *i.e.*, 820 nohm/m for 2005P vs. 980 nohm/m for BCuP-5. The corresponding brazed joint conductivity is ~2-4% that of pure copper.

Effect of Nickel on Brazed Joint Toughness

Presence of nickel in copper-phosphorus brazing filler metals is not desirable because of the formation of brittle nickel phosphide (Ref. 14). The effect of nickel on brazed joint toughness was investigated by examining joint impact values as a function of nickel at constant phosphorus and tin contents of the filler metals.

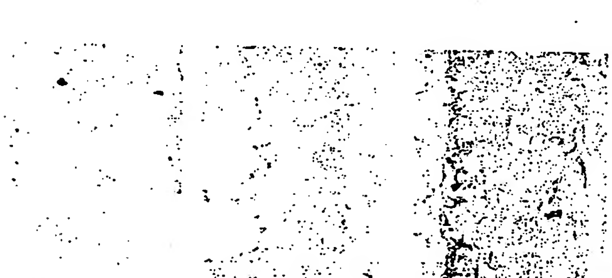
Figure 13 illustrates impact strengths of copper/copper joints brazed with a series of [Cu(1-x)Nix]83P7Sn10 alloys. The nickel content varies from 0 to 15 wt.-%. The highest value of impact strength is observed at ~6 wt.-% Ni, typical of 2005P filler metal. Beyond 6% Ni, there is a precipitous drop in joint toughness.

Figure 14 illustrates changes in brazed joint morphology as a function of filler metal nickel content. To provide a qualitative identification of the phosphide phases present in the brazed joints, SEM elemental maps were generated for joints brazed with a low nickel (6 wt.-% Ni, or 2005P) and a high nickel (15 wt.-% Ni) filler metal. Figure 15 (A-D) illustrates the general morphology and corresponding P, Ni and Cu maps of a 2005P brazed joint. The chunky globular precipitates are rich in copper and phosphorus and are presumably Cu_3P particles with a microhardness of 160HV. Finer particles, several microns in size, are rich in nickel and phosphorus and are presumably Ni_3P with a microhardness of 500HV.

Figure 16 (A-D) shows the same sequence for the high nickel (15 wt-%) filler metal. Elemental maps indicate that large faceted particles are Ni_3P and the finer particles are Cu_3P. From the above data, it is evident that the volume fraction and size of harder Ni_3P phase at the brazed joint increases with the filler metal nickel content. Beyond ~10% Ni, large faceted Ni_3P forms at the brazed joint and reduces the joint toughness. However, at a lower level of nickel, the distribution of Ni_3P is substantially finer and the volume is substantially lower. Finer Ni_3P particles, in this case, act as a strengthening phase and improve joint toughness. Therefore, it appears that nickel, at the optimum level, enhances the joint mechanical properties. This is the case with 2005P.

Effect of Tin On Brazed Joint Microstructure

Presence of tin in the filler metal has been reported to cause base metal erosion at brazed copper joints (Refs. 15,



ɡ. 14 — *Changes in brazed joint morphology due to increase in filler* *etal nickel content (X400)*

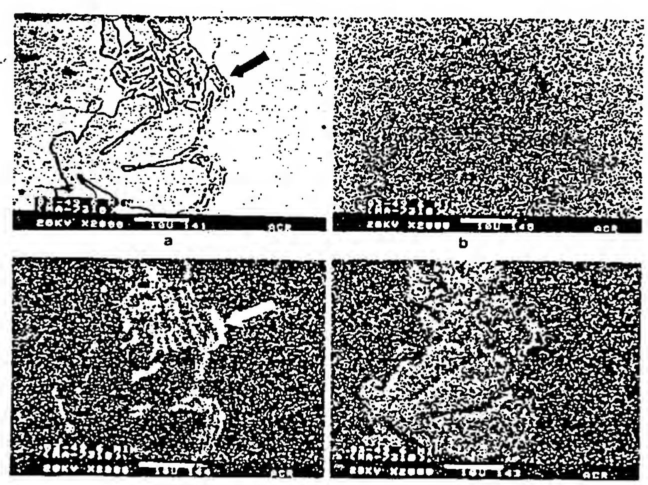


Fig. 15 — Formation of copper phosphide and nickel phosphide particles (arrow) in brazed Cu/2005P/Cu joints. Filler metal nickel content, 5.7%. Joint impact strength, 13.56 J Microhardness of Cu_3P, HV160, and of Ni_3P, HV500

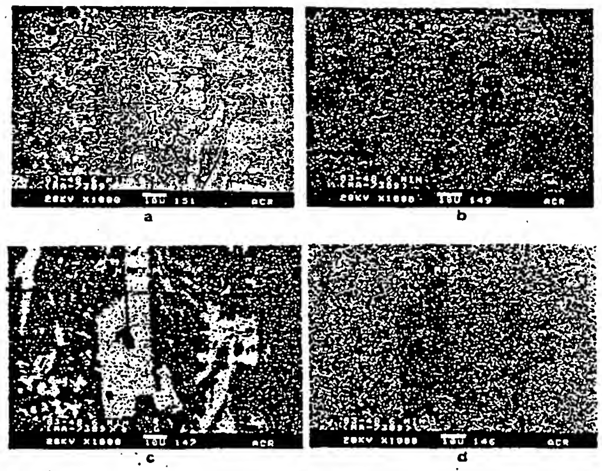


Fig. 16 — Formation of copper phosphide and nickel phosphide particles in brazed Cu/2003P (14.7% Ni)/Cu joints. Joint impact strength, 2.02J. Large faceted particles are Ni_3P with a microhardness of HV500

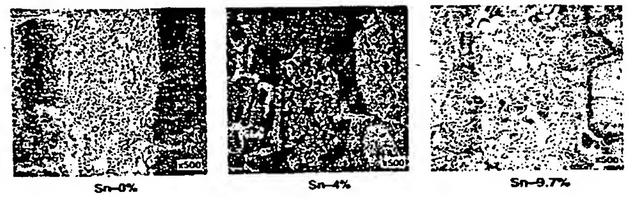


Fig. 17 — Brazed joint morphology as a function of tin content of 2000P series filler metals

16). Figure 17 illustrates the effect of tin content on brazed joint morphology. The copper/copper samples were brazed with a 75 μm (3 mil) clearance at 740°C (1365°F) for 5 minutes. The brazed joint widths or reaction zones are nearly the same for all three alloys with tin content ranging from 0 to 15%. Therefore, within the composition range of tin examined in this study, there is no appreciable difference in base metal erosion. However, the joint interface becomes rough or interlocked with the addition of tin.

Conclusion

A new family of rapidly solidified Cu-Ni-Sn-P brazing filler metals has been developed. The alloys, designated as the MBF 2000P series, are potential replacements for commonly used silver-containing BCuP-5 (15% Ag) and BAg-1 (~40% Ag) in brazing copper and its alloys. Major applications are envisioned to be in heat exchanger, electrical contacts and specialty plumbing.

These new alloys are silver- and cadmium-free, and hence are low in cost and nontoxic. They are self-fluxing and their brazing temperatures are similar to that of BAg-1 and lower than that of BCuP-5. The flow and wetting characteristics of 2000P are superior to those of silver-containing BAg-1 and BCuP-5.

Copper-to-copper brazed joint mechanical properties — tensile, shear and impact strengths — are either similar or superior to those of BCuP-5 and BAg-1 brazed joints. Electrical resistance of joints brazed with 2000P is similar to that of low-silver BCuP-5 brazed joints.

The levels of nickel and tin present in the 2000P series do not adversely affect the joint mechanical properties or base metal erosion. In fact, the nickel content (~6%) in 2005P is found to be optimum for joint toughness.

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